

Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy is a nondestructive technique used for the analysis of compounds that contain magnetic nuclei. Compounds typically examined are those that contain the isotopes ^1H , ^2H , ^{13}C , ^{19}F , ^{27}Al , ^{29}Si , and ^{31}P . Structural, qualitative, and quantitative information can be obtained for both organic and inorganic compounds.

Principle of Technique

For measurement by NMR techniques, the molecule must contain magnetic nuclei. For example, ^{13}C and ^{17}O can be detected by NMR but the more abundant ^{12}C and ^{16}O nuclei cannot. The sample is placed in the coil of a rf-tuned circuit in a magnetic field of strength H . The resonant coil must be tuned to the frequency $\nu = \omega/2\pi$ where $\omega = \gamma H$ and γ is a constant for each magnetic nucleus (42.57 MHz/tesla for protons). The sample is dissolved in an appropriate, usually deuterated, solvent for high-resolution liquid-state NMR or is examined as a fine powder for magic-angle spinning studies. Broad line NMR can be performed on samples as received. An rf pulse of the appropriate frequency is applied to the tuned circuit and the response is monitored in an rf receiver. The response is an exponentially decaying sine wave that is Fourier transformed to yield a spectrum of signal amplitude vs frequency. Samples are characterized by spectra from which chemical shifts, J-coupling splittings, line widths and shapes, and individual relaxation parameters are obtained.

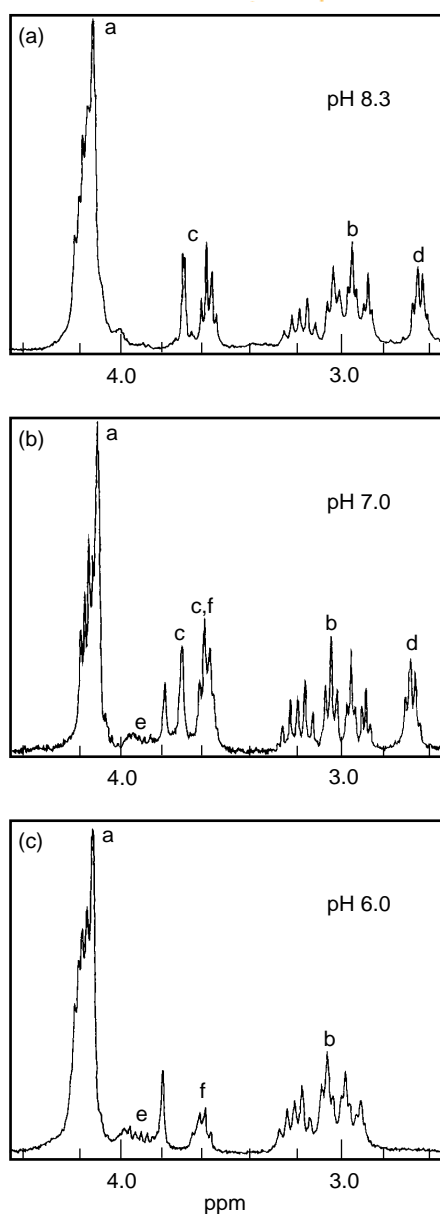
Samples

Form. Liquids, solids, or gases.

Size. Quantities of 1 mg are preferred for liquid-state proton (^1H) NMR but as little as 10 μg can be used. Quantities between 10 and 100 mg

Examples of Applications

- Identification and structure determination of a variety of organic compounds.
- Analysis of solid organic material such as high explosives or rocks from the Nevada Test Site for water content.
- Measurement of coordination type and concentration of silicon atoms in aerogels.
- Determination of silicon and aluminum coordination numbers in zeolites.
- Measurement of phosphorous in metabolites and DNA fragments.



Proton NMR is used to study the dissociation of the lanthanum cryptate of 4,7,13,16,21-pentaoxa-1,10-diazabicyclo [8.8.5] tricosane.

are preferred for liquid-state ^{13}C NMR. Solid-state NMR quantities vary from 20 to 200 mg. In every case, there is an analysis time-sample quantity tradeoff.

Preparation. Samples are dissolved in deuterated solvents for high-resolution liquid-state NMR. Solid samples are ground to uniform particle size for magic-angle spinning experiments. Water can be determined in rocks without extensive sample preparation.

Limitations

Limits of detection vary with the nuclei being examined. Protons (with the exception of tritium) are the most sensitive nuclei; we have detected as little as 5 ng of hydrogen in 10 μg of sample. The sensitivities for fluorine and phosphorous are also high.

Estimated Analysis Time

An average of 15 min is required to obtain a proton spectrum for 1 to 3 mg of material, and 30 to 60 min is required for a ^{13}C spectrum of a 100-mg sample. Detailed structural analysis and quantitation require more time. Dilute solution or solid-state NMR may require overnight data accumulation. The maximum time for data accumulation is usually 48–72 h.

Capabilities of Related Techniques

While FTIR, UV-visible spectrophotometry, and Raman spectroscopy are more sensitive techniques than NMR and give some structural information, they cannot yield the detailed structural or quantitative information provided by NMR. X-ray diffraction spectrometry gives crystal structure information. Gas chromatography-mass spectrometry is useful for the identification and quantitation of analytes in complex mixtures and has better detection limits than NMR.